

## **Supporting Information**

### **Freestanding Metal-Organic Frameworks and Their Derivatives: An Emerging Platform for Electrochemical Energy Storage and Conversion**

Bing He<sup>a†</sup>, Qichong Zhang<sup>b,e\*</sup>, Zhengui Pan<sup>c</sup>, Lei Li<sup>d</sup>, Chaowei Li<sup>h</sup>, Ying Ling<sup>b</sup>, Zhixun Wang<sup>a</sup>, Mengxiao Cheng<sup>g</sup>, Zhe Wang<sup>a</sup>, Yagang Yao<sup>f</sup>, Qingwen Li<sup>b</sup>, Litao Sun<sup>d\*</sup>, John Wang<sup>c,i\*</sup> and Lei Wei<sup>a\*</sup>

a. School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

b. Key Laboratory of Multifunctional Nanomaterials and Smart Systems, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

c. Department of Materials Science and Engineering, National University of Singapore, 117574 Singapore

d. SEU-FEI Nano-Pico Center, Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing, 210096, China

e. Division of Nanomaterials and Jiangxi Key Lab of Carbonene Materials, Jiangxi Institute of Nanotechnology, Nanchang 330200, China

f. College of Engineering and Applied Sciences, and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

g. College of Biomedical Engineering and Instrument Science, Zhejiang University, Hangzhou, 310027, China

h. Henan Key Laboratory of New Optoelectronic Functional Materials, College of Chemistry and Chemical Engineering, Anyang Normal University, 436 Xian'ge Road, Anyang 455000, China

i. Institute of Materials Research and Engineering, A\*Star, Singapore 138634, Singapore

[\*] E-mail: qczzhang2016@sinano.ac.cn; slt@seu.edu.cn; msewangj@nus.edu.sg; wei.lei@ntu.edu.sg

**Table S1. Freestanding MOFs-based/-derived electrodes for Li-based batteries.**

MOF	Sample	Substrate	Preparation strategy	Application	Electrolyte	Capacity	Rate performance	CR/CN	Ref.
ZIF-8	ZnO	No	Electrospinning + annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	896 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	492 mAh g <sup>-1</sup> at 1.5 A g <sup>-1</sup>	91%/100	<sup>1</sup>
Co-MOF	Co-based carbon hybrids	No	assembly +CVD	Anode for LIBs	1 M LiPF <sub>6</sub> OE	763 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	212 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>	92%/550	<sup>2</sup>
ZIF-67	LiCoO <sub>2</sub>	Cu foam	Chemical deposition +annealing	Cathode for LIBs	1 M LiPF <sub>6</sub> OE	155.4 mAh g <sup>-1</sup> at 0.2 C	111.7 mAh g <sup>-1</sup> at 15 C	78.4%/600	<sup>3</sup>
Co-MOF	Co <sub>3</sub> O <sub>4</sub>	NF	Chemical deposition +annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	1226 mAh g <sup>-1</sup> at 1 A g <sup>-1</sup>	543 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>	68%/2000	<sup>4</sup>
ZIF-8	ZnO@NC	CNTs	Chemical deposition +annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	950 mAh g <sup>-1</sup> at 0.05 A g <sup>-1</sup>	400 mAh g <sup>-1</sup> at 1.0 A g <sup>-1</sup>		<sup>5</sup>
Co-MOF	CuV <sub>2</sub> O <sub>6</sub> -Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	Cu foam	Chemical deposition+ ion exchange +annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	1081.9 mAh g <sup>-1</sup> at 0.25 A g <sup>-1</sup>	306.5 mAh g <sup>-1</sup> at 1.75 A g <sup>-1</sup>	~100%/150	<sup>6</sup>
Zn/Co-MOF	ZnCo <sub>2</sub> O <sub>4</sub>	CC	Chemical deposition +annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	2.61 mAh cm <sup>-2</sup> at 0.12 mA cm <sup>-2</sup>	2.05 mAh cm <sup>-2</sup> at 1.2 mA cm <sup>-2</sup>	~100%/100	<sup>7</sup>
ZIF-67	Co <sub>3</sub> S <sub>4</sub>	No	Electrospinning + annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	756 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	592 mAh g <sup>-1</sup> at 1.0 A g <sup>-1</sup>	~100%/200	<sup>8</sup>
Cu-BTC	CuO	3D graphene network	Chemical deposition +annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	395 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	219 mAh g <sup>-1</sup> at 1.6 A g <sup>-1</sup>	~99%/50	<sup>9</sup>
Cu-TCNQ	CuO	Cu foil	Chemical deposition +annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	730 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	367 mAh g <sup>-1</sup> at 1.0 A g <sup>-1</sup>	~92%/150	<sup>10</sup>
ZIF-67	carbon necklace papers	No	Electrospinning + annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	940 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	308 mAh g <sup>-1</sup> at 2.0 A g <sup>-1</sup>	~100%/400	<sup>11</sup>
Co-MOF	Co <sub>3</sub> O <sub>4</sub>	Ti foam plates	Electrodeposition+ annealing	Anode for LIBs	1 M LiPF <sub>6</sub> OE	700 mAh g <sup>-1</sup> at 1.0 A g <sup>-1</sup>	180 mAh g <sup>-1</sup> at 50 A g <sup>-1</sup>	~100%/2000	<sup>12</sup>
CPO-27	CPO-27	NF	Solvothermal method	Anode for LIBs	1 M LiPF <sub>6</sub> OE	670 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	440 mAh g <sup>-1</sup> at 2.0 A g <sup>-1</sup>	93%/500	<sup>13</sup>
ZIF-67	Co/N-PCN@rGO	rGO	Chemical bath deposition +annealing	Cathode for Li-S batteries	1 M LiTFSI + 2.0 wt% LiNO <sub>3</sub> OE	1170 mAh g <sup>-1</sup> at 0.2 C	880 mAh g <sup>-1</sup> at 2 C	~67%/500	<sup>14</sup>
HKUST-T-1	porous carbon polyhedron	No	Filtration + chemical bath deposition +annealing	Cathode for Li-S batteries	1 M LiTFSI + 1.5 wt% LiNO <sub>3</sub> OE	1000 mAh g <sup>-1</sup> at 0.2 C	650 mAh g <sup>-1</sup> at 10 C	97.3%/500	<sup>15</sup>
ZIF-67	ZIF-67	3D monolithic carbon	Chemical bath deposition	Cathode for Li-S batteries	1 M LiTFSI + 0.1 M LiNO <sub>3</sub> OE	1350 mAh g <sup>-1</sup> at 0.05 C	714 mAh g <sup>-1</sup> at 0.05 C	61%/300	<sup>16</sup>
HKUST-T-1	HKUST-1		Chemical bath deposition		1377 mAh g <sup>-1</sup> at 0.05 C	541 mAh g <sup>-1</sup> at 0.05 C	82%/300		
HKUST-T-1	HKUST-1	No	Filtration + chemical bath deposition	Cathode for Li-S batteries	1 M LiTFSI + 1.0 wt% LiNO <sub>3</sub> OE	1102 mAh g <sup>-1</sup> at 0.2 C	449 mAh g <sup>-1</sup> at 10 C	60%/500	<sup>17</sup>

ZIF-8	N-doped porous carbon	No	Filtration + chemical bath deposition +annealing	Cathode for Li-S batteries	1 M LiTFSI + 1.0 wt% LiNO <sub>3</sub> OE	1235 mAh g <sup>-1</sup> at 0.2 C	782 mAh g <sup>-1</sup> at 5 C	64.1%/1800	18
ZIF-8	ZIF-8	carbon nanotube networks	Solvothermal method	Cathode for Li-S batteries	1 M LiTFSI + 1.0 wt% LiNO <sub>3</sub> OE	1480 mAh g <sup>-1</sup> at 0.05 C	840 mAh g <sup>-1</sup> at 1 C	89.3%/500	19
Co-MOF	Co <sub>3</sub> O <sub>4</sub>	CC	Filtration + chemical bath deposition +annealing	Cathode for Li-O <sub>2</sub> batteries	1 M LiTFSI OE	6509 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>			20
ZIF-9	Co <sub>3</sub> O <sub>4</sub>	No	Electrospinning + annealing	Cathode for Li-O <sub>2</sub> batteries	1 M LiCF <sub>3</sub> SO <sub>3</sub> OE	760 mAh g <sup>-1</sup> at 0.8 A g <sup>-1</sup>			21
ZIF-67	Co-NC	CC	Chemical deposition +annealing	Anode for Li-O <sub>2</sub> batteries	1 M LiTFSI + 1.0 wt% LiNO <sub>3</sub> OE				22
Co-MOF	Co-NC	No	3D-printing+ annealing	Cathode for Li-O <sub>2</sub> batteries	0.5 M LiClO <sub>4</sub> OE	1124 mAh g <sup>-1</sup> at 0.05 mA cm <sup>-2</sup>	525 mAh g <sup>-1</sup> at 0.8 mA cm <sup>-2</sup>		23
ZIF-L	3D NC	No	3D-printing+ annealing	Anode for Li-O <sub>2</sub> batteries	1 M LiTFSI + 1.0 wt% LiNO <sub>3</sub> OE				24

CR: capacity retention, CN: cycle number, OE: organic electrolyte.

**Table S2. Freestanding MOFs-based/-derived electrodes for SIBs.**

MOF	Sample	Substrate	Preparation strategy	Application	Electrolyte	Capacity	Rate performance	CR/CN	Ref.
Co-MOF <sub>2</sub>	NC@MoS	CC	Chemical deposition +annealing	Anode for SIBs	1 M NaClO <sub>4</sub> OE	660 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	235 mAh g <sup>-1</sup> at 2.0 A g <sup>-1</sup>	75.3%/1000	<sup>25</sup>
ZIF-67	CoO <sub>x</sub> @NC	No	Electrospinning + annealing	Anode for SIBs	1 M NaClO <sub>4</sub> OE	423 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	141 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>	92.2%/6000	<sup>26</sup>
CuTC NQ	CuTCNQ	carbon nanofibers network	Template-assistance methods	Cathode for SIBs	1 M NaClO <sub>4</sub> OE	252 mAh g <sup>-1</sup> at 0.03 A g <sup>-1</sup>	89 mAh g <sup>-1</sup> at 0.6 A g <sup>-1</sup>	78%/1200	<sup>27</sup>
<u>KNHC F</u>	<u>KNHCF</u>	CNTF	Template-assistance methods	Cathode for SIBs	1 M Na <sub>2</sub> SO <sub>4</sub> AE	58.54 mAh cm <sup>-3</sup> at 0.05 A	42.56 mAh cm <sup>-3</sup> at 5.0 A	90.2%/1000	<sup>28</sup>
<u>KZHC F</u>	<u>KZHCF</u>	CC	Template-assistance methods	Cathode for SIBs	1 M NaClO <sub>4</sub> AE	0.76 mAh cm <sup>-2</sup> at 0.5 A	0.44 mAh cm <sup>-2</sup> at 20 A	87.5%/300	<sup>29</sup>
<u>Na<sub>x</sub>M<sub>n</sub>[Mn(CN)<sub>6</sub>]</u>	<u>Na<sub>x</sub>M<sub>n</sub>[Mn(CN)<sub>6</sub>]</u>	Au-sputtered glass	Electrodeposition	Cathode for SIBs	10 M NaClO <sub>4</sub> AE	85 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>		97%/3000	<sup>30</sup>

Note: Prussian blue and its analogues are marked by undeline.

**Table S3. Freestanding MOFs-based/-derived electrodes for Zn-air batteries.**

MOF	Sample	Substrate	Preparation strategy	Overpotential for OER (10 mA cm <sup>-2</sup> )	HW potential for ORR	Electrolyte	Open-circuit voltage	Voltage gap	Stability	Ref.
ZIF-67	Co <sub>4</sub> N	CC	Chemical deposition + annealing	310 mV	0.8 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.4 V	1.09 V at 50 mA cm <sup>-2</sup> (136 h)	408 cycles	<sup>31</sup>
ZIF	D-ZIF	NF	Chemical deposition + annealing	370 mV	0.6 V	6 M KOH + 0.02 M Zn(Ac) <sub>2</sub> AE	1.38 V	0.78 V at 2 mA cm <sup>-2</sup>	330 h	<sup>32</sup>
Ni-BTC	Ni@N-HCGHF	No	Filtration + annealing	260 mV	0.875 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.49 V		100 cycles	<sup>33</sup>
Co-BTC	Co-N-C	Cobalt plate	Electrodeposition + annealing	310 mV		6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.49 V	~0.63 V at 3 mA cm <sup>-2</sup>	45 cycles	<sup>34</sup>
Co-MOF	NC-Co SA	CC	Chemical deposition + annealing	360 mV	0.87 V	6 M KOH + 0.1 M Zn(Ac) <sub>2</sub> AE	1.411 V	0.45 V at 10 mA cm <sup>-2</sup> (solid)	570 cycles	<sup>35</sup>
CoZn-MOF	P-CoSe <sub>2</sub> /N-C	CC	Chemical deposition + annealing	230 mV	0.87 V	11.25 M KOH + 0.25 M ZnO SE	1.30 V (solid)	~1 V at 1 mA cm <sup>-2</sup> (solid)	~26.7 h (solid)	<sup>36</sup>
ZIF-67	CCVG @CoNT	CC	Chemical deposition + annealing	357 mV	~0.57 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> SE	1.35 V (solid)	1.72 V at 60 mA cm <sup>-2</sup> (solid)	25 h (solid)	<sup>37</sup>
ZIF-L	Co SA@NC F	CNF	Chemical deposition + annealing	400 mV	0.88 V	1.6 M KOH + 0.002 M Zn(Ac) <sub>2</sub> SE	1.41 V (solid)		90 cycles (solid)	<sup>38</sup>
Zn/co-ZIF	HCA-Co	CC	Chemical deposition + annealing	290 mV	0.87 V	11 M KOH + 0.75 M ZnO + 1 M Na <sub>2</sub> SnO <sub>3</sub> + 0.05 M In(OH) <sub>3</sub> SE	1.40 V (solid)		~33.3 h (solid)	<sup>39</sup>
Co-MOF	CoP <sub>x</sub> @CNS	NF	Chemical deposition + annealing	286 mV at 50 mA cm <sup>-2</sup>	0.76 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.40 V	~0.7 V at 5 mA cm <sup>-2</sup> (130 h)	400 cycles	<sup>40</sup>
ZIF-67	Co <sub>3</sub> O <sub>4</sub> -C	NF	Template-assistance method + annealing	310 mV	0.83 V	6 M KOH AE	1.42 V	1.01 V at 30 mA cm <sup>-2</sup>	180 cycles	<sup>41</sup>
ZIF-L	Co <sub>3</sub> O <sub>4</sub> @N-CNMs	CC	Chemical deposition + annealing	310 mV	0.9 V	6 M KOH + 0.1 M Zn(Ac) <sub>2</sub> AE	1.66 V	0.83 V at 5 mA cm <sup>-2</sup>	384 h	<sup>42</sup>
ZIF	CoNCN TF	CNT	Chemical deposition + annealing	380 mV	0.857 V	1.6 M KOH + 0.002 M Zn(Ac) <sub>2</sub> SE	1.34 V (solid)	0.29 V at 0.5 mA cm <sup>-2</sup>	68 cycles	<sup>43</sup>
Co-MOF	NC-Co <sub>3</sub> O <sub>4</sub>	CC	Chemical deposition + annealing	358 mV	0.87 V	11.25 M KOH + 0.25 M ZnO SE	1.44 V (solid)	~0.85 V at 10 mA cm <sup>-2</sup> (solid)	600 cycles (~210 h) (solid)	<sup>44</sup>
KFeCo-PBA	FeCo/Fe CoNi	No	Electrospinning + annealing	378 mV	0.85 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.481 V	0.68 V at 5 mA cm <sup>-2</sup> (240 h)	360 cycle (240 h)	<sup>45</sup>
Co/Mn-ZIF	Co <sub>3</sub> O <sub>4</sub> /Mn <sub>3</sub> O <sub>4</sub> /CN <sub>x</sub>	CNFs	Chemical deposition + annealing	400 mV	0.85 V	6 M KOH AE	1.518 V	1.16 V at 5 mA cm <sup>-2</sup>	50 h	<sup>46</sup>

ZIF-67	Co/N-C	CNFs	Chemical deposition + annealing	~526 mV	0.79 V	6 M KOH AE	1.53 V	~1 V at 5 mA cm <sup>-2</sup>	300 cycles	<sup>47</sup>
ZIF-67	Co/Co-N-C	Carbon felt	Template-assistance method + annealing	310 mV	~0.84 V	6 M KOH + 0.1 M Zn(Ac) <sub>2</sub> AE	1.41 V	0.82 V at 10 mA cm <sup>-2</sup>	1000 cycles	<sup>48</sup>
Co/Fe-MOF	Fe-Co <sub>4</sub> N@N-C	CC	Chemical deposition + conversion method + annealing	390 mV	0.83 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.46 V	~0.8 V at 5 mA cm <sup>-2</sup>	220 cycles	<sup>49</sup>
ZIF-8	Co-N <sub>x</sub> /C	Ti foils	Hydrothermal + annealing	300 mV	0.877 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.42 V	~0.9 V at 50 mA cm <sup>-2</sup>	80 h	<sup>50</sup>
ZIF-67	CoN <sub>x</sub>	Graphe ne aerogel	Chemical deposition + annealing	295 mV	0.83 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.33 V	0.79 V at 50 mA cm <sup>-2</sup>	12 h	<sup>51</sup>
ZIF-L	NC-Co/CoN <sub>x</sub>	CC	Chemical deposition + annealing	289 mV	0.87 V	11.25 M KOH + 0.25 M ZnO SE	1.40 V (solid)		25 h (solid)	<sup>52</sup>
Co-ZIF	NP-Co <sub>3</sub> O <sub>4</sub> /C	CC	Chemical deposition + annealing	~330 mV	0.9 V	6 M KOH AE	1.576 V	1.02 V at 100 mA cm <sup>-2</sup>	400 h	<sup>53</sup>
ZIF-67	Co@NP CFs	CNFs	Chemical deposition + annealing	400 mV	0.66 V	6 M KOH + 0.2 M Zn(Ac) <sub>2</sub> AE	1.44 V	1.16 V at 5 mA cm <sup>-2</sup> (80 h)	480 cycles	<sup>54</sup>
ZIF-67	s-Co@NC P	rGO	Adsorption + annealing		0.81 V	6 M KOH AE	1.466 V		~69 h	<sup>55</sup>

HW: half-wave, SE: solid-state electrolyte, SA: single atom, CNF: carbon nanofiber.

Note: Prussian blue and its analogues are marked by underline

**Table S4. Freestanding MOFs-based/-derived electrodes for Zn-NiCo and ZIBs.**

MOF	Sample	Substrate	Preparation strategy	Application	Electrolyte	Capacity	Rate performance	CR/CN	Ref.
ZIF-67	CoSe <sub>2-x</sub>	CC	Chemical deposition + annealing	Cathode for Zn-Co battery	5 M KOH + 0.02 M Zn(Ac) <sub>2</sub> AE	~11.2 mAh cm <sup>-2</sup> at 4 mA cm <sup>-2</sup>	~7.42 mAh cm <sup>-2</sup> at 10 mA cm <sup>-2</sup>	72.4%/100 00	<sup>56</sup>
Co-MOF	NiCo-DH	NF	Chemical deposition + ion exchange	Cathode for Zn-Ni battery	ZnO saturated 2.5 M KOH AE	329 mAh g <sup>-1</sup> at 0.5 mA cm <sup>-2</sup>	204 mAh g <sup>-1</sup> at 15 mA cm <sup>-2</sup>	73%/850	<sup>57</sup>
Ni-MOF-74	Ni-MOF-74	CNTFs	Solvothermal method	Cathode for Zn-Ni battery	ZnO saturated 2 M KOH AE	184.5 mAh cm <sup>-3</sup> at 0.25 A cm <sup>-3</sup>	147.6 mA h cm <sup>-3</sup> at 5.0 A cm <sup>-3</sup>	86.2%/200 0	<sup>58</sup>
Ag-MOF	Ag	CC	Chemical deposition + annealing	Cathode for Zn-Ag battery	1 M KOH AE	~1,605 mAh cm <sup>-2</sup> at 0.2 mA cm <sup>-2</sup>	~1.32 mAh cm <sup>-2</sup> at 2 mA cm <sup>-2</sup>	90%/70	<sup>59</sup>
Ni-MOF	Ni-MOF	CNTF	Solvothermal method	Cathode for Zn-Ni battery	ZnO saturated 2 M KOH AE	0.4 mAh cm <sup>-2</sup> at 0.5 mA cm <sup>-2</sup>	0.315 mAh cm <sup>-2</sup> at 5 mA cm <sup>-2</sup>	89%/600	<sup>60</sup>
Mn-MIL-100	Mn <sub>2</sub> O <sub>3</sub> @C	CNTF	Solvothermal method + annealing	Cathode for ZIBs	2 M ZnSO <sub>4</sub> + 0.5 M MnSO <sub>4</sub> AE	154.9 mAh cm <sup>-3</sup> at 0.3 A cm <sup>-3</sup>	90.3 mAh cm <sup>-3</sup> at 3.0 A cm <sup>-3</sup>	79.6%/300 0	<sup>61</sup>
V-MIL-47	V-MIL-47	CNTF	Solvothermal method	Cathode for ZIBs	2 M ZnCl <sub>2</sub> AE	101.8 mAh cm <sup>-3</sup> at 0.1 A cm <sup>-3</sup>	65.5 mAh cm <sup>-3</sup> at 5.0 A cm <sup>-3</sup>	84.6%/400	<sup>62</sup>
Mn-MOF	Od-Mn <sub>3</sub> O <sub>4</sub> @C	CC	Solvothermal method + annealing	Cathode for ZIBs	2 M ZnSO <sub>4</sub> + 0.2 M MnSO <sub>4</sub> AE	396.2 mAh g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	143 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>	95.7%/120 00	<sup>63</sup>

**Table S5. Freestanding MOFs-based/-derived electrodes for supercapacitors.**

MOF	Sample	Substrate	Preparation strategy	Electrolyte	Potential window	Capacitance	Rate performance	CR/CN	Ref.
ZIF-L	Ni/Co-N	CC	Chemical deposition + annealing	1 M KOH AE	0-0.5 V	361.93 C g <sup>-1</sup> at 2 mA cm <sup>-2</sup>	207.6 C g <sup>-1</sup> at 50 Ma cm <sup>-2</sup>		64
Co-MOF	ZnCo <sub>2</sub> O <sub>4</sub> @NC	Carbon textiles	Chemical deposition + ion exchange + annealing	3 M KOH AE	-0.5-4.5 V	2.244 F cm <sup>-2</sup> at 2 Ma cm <sup>-2</sup>	1.676 F cm <sup>-2</sup> at 64 Ma cm <sup>-2</sup>	~99.37%/10000	65
Co-MOF	P-Co <sub>3</sub> O <sub>4</sub> @P NC	Carbon fibers	Chemical deposition + annealing	2 M KOH AE	0-0.4 V	1.023 F cm <sup>-2</sup> at 1 Ma cm <sup>-2</sup>	0.806 F cm <sup>-2</sup> at 30 Ma cm <sup>-2</sup>	96.9%/1000	66
Ni-HITP	Ni-HITP	CNFs	Hydrothermal method + filtration	3 M KCl AE	0-0.7 V	125 F g <sup>-1</sup> at 0.33 A g <sup>-1</sup>	87.5 F g <sup>-1</sup> at 33 A g <sup>-1</sup>		67
Cu-CAT	Cu-CAT	Carbon papers	Chemical deposition	3 M KCl AE	0-0.5 V	202 F g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	134 F g <sup>-1</sup> at 10 A g <sup>-1</sup>	80%/5000	68
ZIF-8	NC	No	Electrospinning + annealing	2 M H <sub>2</sub> SO <sub>4</sub> AE	0-1 V	307.2 F g <sup>-1</sup> at 1.0 A g <sup>-1</sup>	193.4 F g <sup>-1</sup> at 50.0 A g <sup>-1</sup>	98.2%/1000	69
Co-MOF	Cu(Co-Ni) <sub>2</sub> S <sub>4</sub>	NF	Chemical deposition + ion exchange + annealing	1 M KOH AE	0-0.4 V	0.38 mAh cm <sup>-2</sup> at 2 Ma cm <sup>-2</sup>	0.2 mAh cm <sup>-2</sup> at 30 Ma cm <sup>-2</sup>	96.2%/5000	70
Cu-CAT	Cu-CAT	Ppy	Hydrothermal method	3 M KCl AE	0-0.5 V	116 F g <sup>-1</sup> at 1.25 Ma cm <sup>-2</sup>	71 F g <sup>-1</sup> at 25 Ma cm <sup>-2</sup>	87%/5000	71
CoNi-MOF	CoNi-MOF	Carbon paper	Template-assistance method	1 M KOH AE	0-0.45 V	1044 F g <sup>-1</sup> at 2 A g <sup>-1</sup>	569 F g <sup>-1</sup> at 32 A g <sup>-1</sup>		72
MIL-88-Fe	S-a-Fe <sub>2</sub> O <sub>3</sub> @C	CNTFs	Solvothermal method + annealing	1 M Na <sub>2</sub> SO <sub>4</sub> AE	-1.0-0 V	1.23 F cm <sup>-2</sup> at 2 Ma cm <sup>-2</sup>	0.78 F cm <sup>-2</sup> at 20 Ma cm <sup>-2</sup>	97.6%/4000	73
Co-MOF	NiCo <sub>2</sub> O <sub>4</sub>	CC	Chemical deposition + ion exchange + annealing	2 M KOH AE	0-0.6 V	1055.3 F g <sup>-1</sup> at 2.5 Ma cm <sup>-2</sup>	483.3 F g <sup>-1</sup> at 60 Ma cm <sup>-2</sup>		74
ZIF-67	Porous carbon	No	Electrospinning + annealing	2 M H <sub>2</sub> SO <sub>4</sub> AE	0-1.0 V	421 F g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	264 F g <sup>-1</sup> at 20 A g <sup>-1</sup>		75
CoNi-MOF	CoNi-MOF	Ni film	Template-assistance method + solvothermal method	6 M KOH AE	0-0.5 V	813 C cm <sup>-3</sup> at 0.5 A cm <sup>-3</sup>	325 C cm <sup>-3</sup> at 5 A cm <sup>-3</sup>		76
Ni-MOF	Ni-MOF	CC	Solvothermal method	2 M KOH AE	0-0.4 V	208.8 mAh g <sup>-2</sup> at 2 Ma cm <sup>-2</sup>	142.4 mAh g <sup>-2</sup> at 20 Ma cm <sup>-2</sup>		77
CuCo-MOF	Cu-Co <sub>9</sub> S <sub>8</sub>	NF	Template-assistance method + solvothermal method	6 M KOH AE	0-0.5 V	2636 F g <sup>-1</sup> at 2 A g <sup>-1</sup>	1584 F g <sup>-1</sup> at 30 A g <sup>-1</sup>	94%/5000	78
UiO-66	UiO-66	Carbon fibers	electrodeposition	3 M KCl AE	-0.4-0.6 V	15 Mf cm <sup>-1</sup> at 5 Mv s <sup>-1</sup>	8 Mf cm <sup>-1</sup> at 100 Mv s <sup>-1</sup>	96%/1200	79
ZIF-67	Co <sub>3</sub> O <sub>4</sub> /NC	CC	Chemical vapor method + annealing	6 M KOH AE	0-0.5 V	1.22 F cm <sup>-2</sup> at 0.5 Ma cm <sup>-2</sup>	0.72 F cm <sup>-2</sup> at 20 Ma cm <sup>-2</sup>	98.2%/4000	80
Co-ZIF	NiCo-LDH	Carbon foam	Chemical deposition + ion exchange	2 M KOH AE	0-0.5 V	756 C g <sup>-1</sup> at 0.5 A g <sup>-1</sup>	414 C g <sup>-1</sup> at 20 A g <sup>-1</sup>	81.7%/5000	81
Co-Ni-	Co <sub>3</sub> O <sub>4</sub> -	Graphene	Chemical deposition +	2 M KOH	0.1-0.4 V	783 F g <sup>-1</sup> at 530 F g <sup>-1</sup> at 10		84%/5000	82

CMF	NiO	foam	annealing	AE		0.5 A g <sup>-1</sup>	A g <sup>-1</sup>		
Zn/Co-ZIF-L	Zn <sub>0.76</sub> Co <sub>0.24</sub> S/NiCo <sub>2</sub> S <sub>4</sub>	CC	Chemical deposition + ion exchange + annealing	2 M KOH AE	0-0.5 V	2674 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	2112 F g <sup>-1</sup> at 20 A g <sup>-1</sup>	93%/2000	<sup>83</sup>
Co-MOF	Co-MOF	CC	Chemical deposition + ion exchange	1 M LiOH	0-0.5 V	803 F g <sup>-1</sup> at 0.5 Ma cm <sup>-2</sup>	415 F g <sup>-1</sup> at 15 Ma cm <sup>-2</sup>	90%/15000	<sup>84</sup>
Mn-BTC	Mn <sub>2</sub> O <sub>3</sub>	graphene network	Chemical deposition + annealing	0.5 M Na <sub>2</sub> SO <sub>4</sub> AE	0-0.8 V	471.1 F g <sup>-1</sup> at 0.2 A g <sup>-1</sup>	270.0 F g <sup>-1</sup> at 5 A g <sup>-1</sup>	~100%/1800	<sup>85</sup>
Co-MOF	CoSe <sub>2</sub> /NC	NF	Chemical deposition + annealing	6 M KOH AE	0-0.35 V	120.2 mAh g <sup>-2</sup> at 1 A g <sup>-1</sup>	73.6 mAh g <sup>-2</sup> at 20 A g <sup>-1</sup>	92%/10000	<sup>86</sup>
HKUST-1	Porous carbon	No	Filtration + annealing	6 M KOH AE	-1.1 - -0.1 V	194.8 F g <sup>-1</sup> at 2 A g <sup>-1</sup>	120.9 F g <sup>-1</sup> at 100 A g <sup>-1</sup>	95%/10000	<sup>87</sup>
ZIF-L	NC	Carbon foam	Chemical deposition + annealing	6 M KOH AE	-1- 0 V	238 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	194.8 F g <sup>-1</sup> at 2 A g <sup>-1b</sup>		<sup>88</sup>
Co-MOF	Co <sub>3</sub> O <sub>4</sub> /C	NF	Hydrothermal method + annealing	3 M KOH AE	-0.1-0.4 V	776.5 F g <sup>-1</sup> at 1 Ma cm <sup>-2</sup>	635.3 F g <sup>-1</sup> at 20 Ma cm <sup>-2</sup>	96%/2000	<sup>89</sup>
Co/Zn-MOF	Co/Zn-S	No	Filtration + annealing	6 M KOH AE	0-0.5 V	1640 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	1076.4 F g <sup>-1</sup> at 10 A g <sup>-1</sup>		<sup>90</sup>
Mn-MOF	Mn-MOF	NF	Solvothermal method	2 M KOH AE	0-0.6 V	567.5 mAh g <sup>-2</sup> at 1 A g <sup>-1</sup>	317.5 mAh g <sup>-2</sup> at 12 A g <sup>-1</sup>	92.3%/5000	<sup>91</sup>
ZIF-67	NiCo <sub>2</sub> S <sub>4</sub>	NF	Chemical deposition + ion exchange + Hydrothermal method	6 M KOH AE	0-0.4 V	939 C g <sup>-1</sup> at 1 A g <sup>-1</sup>	712 C g <sup>-1</sup> at 10 A g <sup>-1</sup>	92.8%/5000	<sup>92</sup>
	CoS <sub>2</sub>		Chemical deposition + Hydrothermal method + annealing		-1.1 - -0.3 V	343.5 C g <sup>-1</sup> at 1 A g <sup>-1</sup>	146.3 C g <sup>-1</sup> at 20 A g <sup>-1</sup>		
Co-MOF	NiCo-A-S	CC	Chemical deposition + ion exchange + annealing + Hydrothermal method	3 M KOH AE	0-0.5 V	213 mAh g <sup>-2</sup> at 1 A g <sup>-1</sup>	171 mAh g <sup>-2</sup> at 20 A g <sup>-1</sup>	86%/5000	<sup>93</sup>
Ni-MOF	NiCoS	NF	Hydrothermal method	1 M KOH AE	0-0.4 V	2815.4 F g <sup>-1</sup> at 1 Ma cm <sup>-2</sup>	1053.6 F g <sup>-1</sup> at 30 Ma cm <sup>-2</sup>	43%/3000	<sup>94</sup>
Co-MOF	NiCo-LDH /Co <sub>9</sub> S <sub>8</sub>	CC	Chemical deposition + ion exchange + Hydrothermal method	6 M KOH AE	0-0.4 V	2850 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	2063 F g <sup>-1</sup> at 10 A g <sup>-1</sup>	92.6%/500	<sup>95</sup>
Co-MOF	Co <sub>3</sub> O <sub>4</sub>	CC	Chemical deposition + electrochemical oxidation	1 M KOH AE	0-0.45 V	226.1 C g <sup>-1</sup> at 1.3 A g <sup>-1</sup>	219.6 C g <sup>-1</sup> at 8.9 A g <sup>-1</sup>	77%/5000	<sup>96</sup>
Co-MOF	CoMoO <sub>4</sub>	NF	Solvothermal method + ion exchange	3 M KOH AE	0-0.5 V	12.2 F cm <sup>-2</sup> at 2 Ma cm <sup>-2</sup>	10 F cm <sup>-2</sup> at 50 Ma cm <sup>-2</sup>	90.5%/500	<sup>97</sup>
ZIF-67	CoS <sub>2</sub>	Cu foam	Chemical deposition + annealing + chemical bath	6 M KOH AE	0-0.4 V	2185 F g <sup>-1</sup> at 1 Ma cm <sup>-2</sup>	1785 F g <sup>-1</sup> at 50 Ma cm <sup>-2</sup>	~100%/1000	<sup>98</sup>
Zn/Co-MOF	Zn-Co-P	NF	Chemical deposition + annealing	6 M KOH AE	0-0.45 V	2115.5 F g <sup>-1</sup> at 1 A g <sup>-1</sup>	1086.5 F g <sup>-1</sup> at 50 A g <sup>-1</sup>	80.3%/7000	<sup>99</sup>

**Table S6. Freestanding MOF based electrodes for HER and OER.**

MOF	Sample	Substrate	Preparation strategy	Electrolyte	application	Onset potential/V	Overspotential/mV	Tafel/ mV dec <sup>-1</sup>	Stability	Ref.
NiCo-BDC	NiCo-BDC	NF	Template-assistance method	1 M KOH AE	OER		230	61	24 h	100
MOF-74-Co/Fe	CoFe <sub>2</sub> O <sub>4</sub> /C	NF	Solvothermal method + annealing	1 M KOH AE	OER	1.45	240	45	0.42%/30 h	101
FeCo <sub>0.5</sub> Ni <sub>0.5</sub> -MOF	FeCo <sub>0.5</sub> Ni <sub>0.5</sub> -LDH	Cu foil	Chemical deposit + ion exchange	1 M KOH AE	OER		248	38	50 h	102
Co-BDC	Co <sub>3</sub> O <sub>4</sub> /C	Ni foil	Solvothermal method + annealing	1 M KOH AE	OER		208	50.1	36 h	103
Cu-TDC	Cu <sub>2</sub> O-S/C	Cu foil					313	65.6	60	
Co-MOF	Co <sub>3</sub> O <sub>4</sub> /C	Cu foil	Chemical deposit + annealing	0.1 M KOH AE	OER	1.47	290	70	6.5%/30 h	104
Fe/Ni/Co-MIL-53	Fe/Ni/Co-MIL-53	NF	Solvothermal method	1 M KOH AE	OER		219	53.5	1000 cycles	105
MIL-53(FeNi)	MIL-53(FeNi)	NF	Solvothermal method	1 M KOH AE	OER		233 (50 mA cm <sup>-2</sup> )	39.6	~13.3 h	106
<u>KNi[Fe(CN)<sub>6</sub>]<sub>2</sub>P(O)O<sub>2</sub></u>	Ni <sub>2</sub> P/(NiF <sub>3</sub> ) <sub>2</sub> P(O)O <sub>2</sub>	NF	Template-assistance method + annealing	1 M KOH AE	OER		150	60	50 h	107
CoNi-MOF	CoNi-MOF	NF	Solvothermal method	1 M KOH AE	OER	1.41	215	51.6	300 h	108
Fe/Ni-BTC	Fe/Ni-BTC	NF	Electrodeposition	0.1 M KOH AE	OER	1.40	270	47	15 h	109
ZnCo-MOF	Zn-CoSe <sub>2</sub>	CC	Chemical deposit + annealing	1 M KOH AE	OER	~1.35	356	88	1%/14 h	110
Ni-BDC	Ni-BDC @NiS	NF	Solvothermal method	1 M KOH AE	OER	1.52	340 (20 mA cm <sup>-2</sup> )	62	12 h	111
<u>NiFe-PBA</u>	Fe-NiO	CC	Template-assistance method + annealing	1 M KOH AE	OER		218	47	50 h	112
Co-MOF	CoSe <sub>2</sub> /C	CC	Chemical deposit + annealing	0.5 M H <sub>2</sub> SO <sub>4</sub> AE	HER		84	38	72 h	113
Co-MOF	W-CoP	CC	Ion exchange + annealing	0.5 M H <sub>2</sub> SO <sub>4</sub> AE	HER	0.031	89	58	36 h	114
CoW-MOF	S-CoWP @S,N-C	CC	Solvothermal method + annealing	0.5 M H <sub>2</sub> SO <sub>4</sub> AE	HER		146	68	3%/40 h	115
NiRu-MOF	NiRu-MOF	NF	Solvothermal method	1 M KOH AE	HER		156	90	24 h	116
Co-MOF	Mo-CoP/NC	Ti foil	Chemical deposit + ion exchange + annealing	0.5 M H <sub>2</sub> SO <sub>4</sub> AE	HER	0.004	59	51.2	24 h	117
Ni-ZIF	Ni-ZIF/Ni-B	NF	Hydrothermal + chemical bath	1 M KOH AE	OER HER		234	57	36 h	118
<u>Co-Fe-PBA</u>	Fe-CoP	NF	Chemical deposit + annealing	1 M KOH AE			67	108	64 h	
Co-MOF	Mo-CoP	CC	Ion exchange + annealing	1 M KOH AE	OER HER		190	36	30 h	119
NiFe-	NiFe-	NF	Solvothermal method	1 M KOH AE			78	92	30 h	
Co-MOF	Mo-CoP	CC	Ion exchange + annealing	1 M KOH AE	OER		305	56	20 h	120
					HER		40	65	20 h	
NiFe-	NiFe-	NF	Solvothermal method	1 M KOH AE	OER		230 (50 mA cm <sup>-2</sup> )	32	17 h	121

MOF	MS/MOF						mA cm <sup>-2</sup> )				
							HER	OER	309	53	3000
ZIF-67	CoNC	NF	Template-assistance method + annealing	1 M KOH AE	HER	OER	309	53	3000	cycles	122
NiFe-MOF	NiFe-MOF	NF	Hydrothermal method		HER	OER	190	98			
CoFe-PBA	CoFe-PBA	NF	Hydrothermal method	0.1 M KOH AE	HER	OER	240	34	~5.6 h	2000 s	123
ZIF-67	CNT	NF	Electrodeposition + annealing		HER	OER	134				
CPO-27-Ni	CPO-27-Ni	NF	Template-assistance method + annealing	1 M KOH AE	HER	OER	256	54	24 h	124	
Co-MOF	CoP	NF	Chemical deposit + ion exchange + annealing		HER	OER	48	66			
Co-MOF	NC-CNT/CoP	CC	Chemical deposit + annealing	1 M KOH AE	HER	OER	286	62	~6 h	125	
NiFe-MOF	NiFe-MOF	NF	Solvothermal method		HER	OER	133	96			
Co-MOF	Co-Pt/C	CC	Chemical deposit + annealing	1 M KOH AE	HER	OER	295	52	0.3%/30 h	3.7%/30 h	126
FeCo-PBA	FeCo/C FeCoP/C	NF	Template-assistance method + annealing		HER	OER	49.48	74			
Co-MOF	Ni <sub>2</sub> P-Co <sub>2</sub> P@C	NF	Chemical deposit + ion exchange + annealing	1 M KOH AE	HER	OER	317 (50 mA cm <sup>-2</sup> )	65.6	12 h	15 h	127
Ni-9AC-AD	Ni-9AC-AD	NF	Hydrothermal method		HER	OER	41.1	65.3			
					HER	OER	240		20 h	15%/20 h	128
					HER	OER	120	73			
					HER	OER	198	30.6	40 h	50 h	129
					HER	OER	142	94.7			
					HER	OER	320	72	10 h	10 h	130
					HER	OER	0.035	50	46		
					HER	OER	219	74		107	131
					HER	OER	55	107			
					HER	OER	290 (50 mA cm <sup>-2</sup> )	64	20 h	20 h	132
					HER	OER	167 (50 mA cm <sup>-2</sup> )	68			
					HER	OER	350 (50 mA cm <sup>-2</sup> )	51.3	30 h	30 h	133
					HER	OER	143	79.5			

PKi: phosphate solution.

Note: Prussian blue and its analogues are marked by underline

**Table S7** Comparisons between freestanding electrodes and traditional powder-form electrodes

Differences	Freestanding MOF based electrodes	Traditional power-form MOF based electrode
<b>Electrode preparation</b>	MOF-based active materials grown on conductive substrates or formed a freestanding film directly as electrodes.	MOF-based active materials coated on conductive substrates by slurry-coating methods.
<b>Additives</b>	No	Unactive binders and conductive additives
<b>Substrate selections</b>	Diversification. 1D: carbon nanotube fibers; 2D: carbon cloths, carbon papers, metal foils; 3D: nickel foams, 3D graphene foam	Limited selections. 2D Al/Cu foils or carbon cloths as main option
<b>Electrode configuration</b>	(i) Nanorod/sheets/wires/wall arrays (ii) 3D architecture with porous structure	Thin film form without ordered nanostructure arrays
<b>Active sites</b>	Abundant and accessible active sites	Limited active sites due to the coverage of polymer binders and the stacking of active materials
<b>Ion diffusion</b>	3D nanostructure arrays or porous structures for fast ion diffusion	Dense accumulation for sluggish ion diffusion rate
<b>Electron transportation</b>	Seamless contact between active materials and conductive substrates or 3D continuous conductive network for fast electron transportation	Interspersion of insulating adhesive and poor contact between active materials and conductive substrates resulting in large electron transfer resistance
<b>Stability for energy storage</b>	Enough free space accommodating volume expansion of active materials during charge-discharge process to restrain the decay of the capacity	Easily falling off during the cycle test due to the dense electrode configuration
<b>Stability for OER and ORR</b>	Stable, owing to the strong adhesion with substrates and open array structures	Easily falling off with the generation of gas bubbles owing to the poor contact with substrates
<b>Mechanism research</b>	Accurate platform to study the transformation of substances during the energy storage and conversion due to the absence of additives	Existence of interference in the precise study of the structures, valences and performances of active materials due to the introduction of conductive agents and binders
<b>Wearable application</b>	Good mechanical flexibility due to the existence of the space among nanostructure units and seamless contact with the flexible substrates	Poor mechanical flexibility because of the easily cracking and peeling of active materials after bending multiple times

**Table S8** Electrochemical applications and the corresponding properties required.

Applications	Required properties	Freestanding MOFs (PBAs)	Freestanding MOF derivatives
Li/Na/Zn-ion Batteries	➤ Abundant redox active sites; ➤ Regular channels and porous structure; ➤ Excellent conductivity.	CPO-27, KZHCF (PBAs), CuTCNQ	ZnO (ZIF-8), Co <sub>3</sub> O <sub>4</sub> (ZIF-67), Mn <sub>2</sub> O <sub>3</sub> @C (Mn-MIL-100)
Li/Zn-air batteries	➤ Nanostructure active species (nitrides, cardides, oxides, and metal atoms) for OER and ORR; ➤ Excellent conductivity and porous structure.	D-ZIF	NC-Co/CoNx (ZIF-L), NC-Co <sub>3</sub> O <sub>4</sub> (Co-MOF), Co-NC (ZIF-67)
Li-S batteries	➤ Hindering the shuttle effect of soluble LiPSs; ➤ High pore volume to accommodate volume variation; ➤ Excellent conductivity.	ZIF-67, HKUST-1, ZIF-8	N-doped porous carbon (ZIF-8), Co/N-PCN@rGO (ZIF-67)
Supercapacitors	➤ Abundant redox active sites; ➤ Large accessible surface areas; ➤ Excellent conductivity.	Ni-HITP, Cu-CAT, UiO-66	NiCo <sub>2</sub> O <sub>4</sub> (Co-MOF), Mn <sub>2</sub> O <sub>3</sub> (Mn-BTC), Co <sub>3</sub> O <sub>4</sub> (ZIF-67)
Electrochemical water splitting	➤ Nanostructure active species (nitrides, cardides, oxides, and metal atoms) for OER and HER; ➤ Excellent conductivity and porous structure.	NiCo-BDC, MIL-53 (FeNi), CoFe-PBA, Fe/Ni-BTC	Fe-NiO (NiFe-PBA), Mo-CoP (Co-MOF), CoNC (ZIF-67)

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